

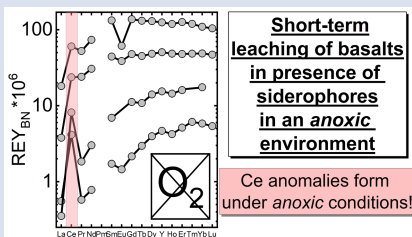
# Siderophores and the formation of cerium anomalies in anoxic environments

D. Kraemer<sup>1,2\*</sup>, M. Bau<sup>1</sup>



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## Abstract



Microbes and plants affect the mobility of trace elements and may have done so since the onset of “life” on Earth. The recognition of such bio-effects on early Earth or Mars remains challenging and the impact of organisms on element mobilisation and redox cycling is largely unconstrained. Redox-sensitive trace elements, such as Ce, are used as geochemical proxies for reconstructing atmospheric oxygen levels, but bio-proxies are still largely lacking. We show that experimental water–rock interaction in presence of siderophores, globally abundant biogenic ligands excreted by microbes, fungi and plants, enhances lanthanoide mobilisation and produces positive Ce anomalies even under strictly anoxic conditions. This is the first evidence for bio-mediated

oxidation of Ce and Ce anomaly formation in anoxic environments. Oxygen-independent fractionation of Ce from its redox-insensitive rare earth element neighbours during geo–bio interaction may hold the potential to use Ce anomalies as a bio-proxy in addition to its current use as a redox proxy.

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## Introduction

Cerium belongs to the lanthanoides, which, together with the pseudolanthanoid Y, are referred to as “rare earth elements and yttrium” (REY). The REY show coherent behaviour in the natural environment due to their similar charge and systematically decreasing ionic radii. Cerium is an exception, as it can be oxidised to Ce(IV) and hence decoupled from its redox-insensitive, strictly trivalent REY neighbors La and Pr. During pedogenesis and oxidative weathering, Ce(IV) may form insoluble cerianite (CeO<sub>2</sub>) which remains fixed in the regolith when the REY(III) are gradually mobilised (Braun *et al.*, 1990), eventually producing Ce anomalies in normalised REY patterns of soil. Likewise, Fe and Mn-oxhydroxides have the tendency to surface-oxidise Ce upon sorption, facilitating positive Ce<sub>N</sub> anomalies at the mineral surfaces and, with time, progressively more negative anomalies in the associated (pore) solutions (Bau and Koschinsky, 2009). Due to their particle reactivity and the presumed immobility of REY, presence or absence of Ce anomalies in palaeoweathering profiles and marine chemical sediments are commonly used as a robust qualitative redox proxy (*e.g.*, German and Elderfield, 1990; Riding *et al.*, 2014).

Biota facilitates a strong control on redox-sensitive elements, such as Fe (*e.g.*, Byrne *et al.*, 2015). A class of biogenic ligands that interacts strongly with oxide and silicate minerals (Brantley *et al.*, 2001; Kraemer *et al.*, 2014) and that solubilises Fe, REY and other high field strength elements (Yoshida *et al.*, 2004; Christenson and Schijf, 2011; Bau *et al.*, 2013; Kraemer *et al.*, 2015, 2017) are the so-called “siderophores”. These are excreted by bacteria, plants and fungi, primarily to mobilise

bioessential Fe (Haas, 2003) and to cope with metal toxicity (Braud *et al.*, 2010). Siderophore-promoted oxidation of Ce under oxic conditions has been described in literature (Brantley *et al.*, 2001; Yoshida *et al.*, 2004; Bau *et al.*, 2013; Kraemer *et al.*, 2015, 2017).

This study fills the important knowledge gap on the impact of the oxygen level of a system on this process. The naturally abundant microbial siderophore desferrioxamine B (DFOB), produced by *Streptomyces pilosus*, and the fungal siderophore desferrichrome (DFC), produced by *Ustilago sphaerogena*, are used as model siderophores for batch incubation experiments with powdered igneous rocks to simulate water–rock interaction (WRI) at oxygen levels of (i) 0 ppmv O<sub>2</sub> (‘anoxic’), (ii) 0.1 % O<sub>2</sub> (‘hypoxic’) and (iii) ~21 % O<sub>2</sub> (present atmospheric level; ‘oxic’). The experiments were conducted at room temperature in a gloveless anaerobic chamber with various sampling times and a fixed rock/water ratio of 20 g/L.

## Results

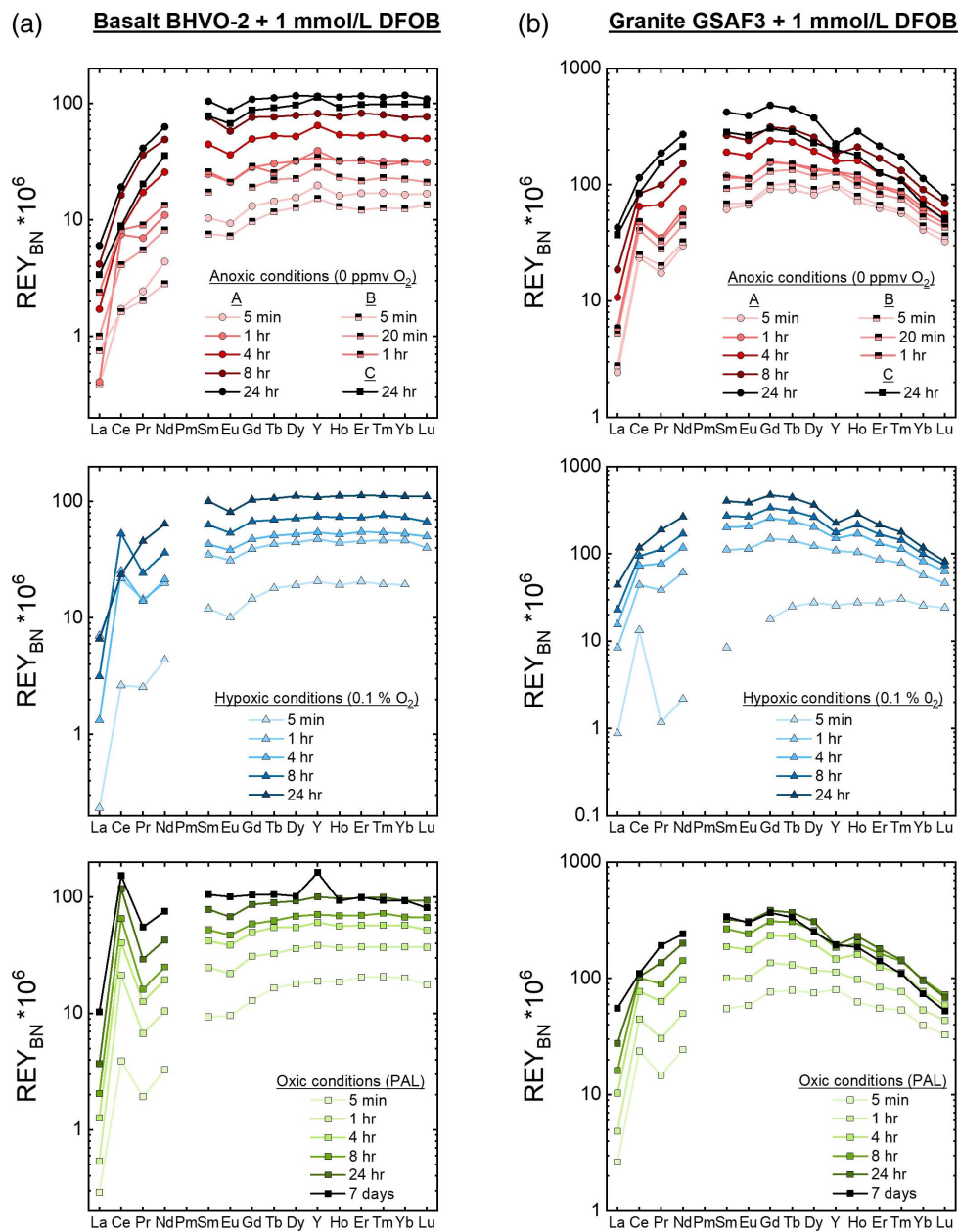
A set of igneous rocks, comprised of mid-ocean ridge basalt (MORB; glass and microcrystalline), island-arc basalt (IAB), andesite and granite, was chosen for investigating WRI at different atmospheric conditions. Concentrations of REY in leachates were normalised to those in the respective bulk rock (subscript “BN”) to facilitate comparison between mobilised REY relative to the bulk rock inventory. We emphasise that the rock samples were pristine and that the bulk rock REY patterns (Fig. S-1) did not show any signs of alteration.

1. Department of Physics and Earth Sciences, Jacobs University Bremen, Campus Ring 1, 28759 Bremen, Germany

2. Current address: Federal Institute for Geosciences and Natural Resources (BGR), Stilleweg 2, 30655 Hannover, Germany

\* Corresponding author (email: [dennis.kraemer@bgr.de](mailto:dennis.kraemer@bgr.de))





**Figure 1** REY<sub>BN</sub> patterns of time series experiments with (a) basalt and (b) granite.

Figures 1–3 show REY<sub>BN</sub> patterns of the leaching experiments at different run times, and Figure 4 shows calculated Ce anomalies ( $Ce_{CN}/Ce_{CN}^*$ ) vs. Y/Ho ratio of the anoxic (shades of red, circles), hypoxic (shades of blue, triangles) and oxic experiments (shades of green, squares). Leaching of REY from igneous rocks in the presence of either of the two model siderophores under the three studied  $pO_2$  conditions revealed the following:

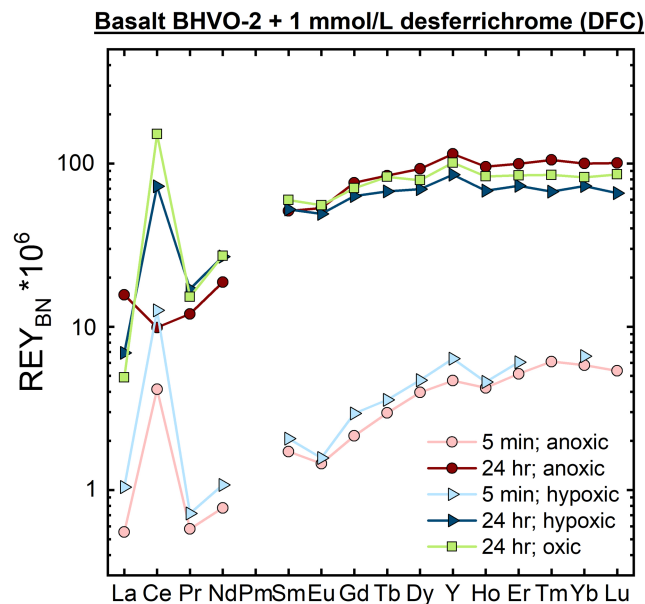
- (i) the amount of mobilised REY increases with time;
- (ii) HREY mobilisation is stronger than LREY mobilisation, especially La is depleted;
- (iii) patterns of the anoxic to oxic experiments at the same time interval are similar, except for Ce, and corroborate published data from oxic experiments (Kraemer *et al.*, 2015);
- (iv) in the first 5 min of leaching, positive  $Ce_{BN}$  anomalies develop even under strictly anoxic conditions, regardless of mineralogical composition, texture and REY

concentrations of the rock sample; after 60 min at the latest, these  $Ce_{BN}$  anomalies become smaller, and later disappear in all anoxic experiments, resulting in patterns without  $Ce_{BN}$  anomaly after 24 hr;

- (v) positive  $Ce_{BN}$  anomalies formed in all hypoxic and oxic experiments after at least 5 min, except in experiments with glassy MORB and granite. Nevertheless, the  $Ce_{BN}$  anomalies that formed during the hypoxic experiments are less pronounced than those that developed during the oxic experiments, suggesting that  $pO_2$  exerts a control on the formation of Ce anomalies during WRI with siderophores;
- (vi) Y-Ho fractionation was more pronounced in the anoxic experiments than in the other experiments (Fig. 4).

In the course of individual experiments, pH first decreased from 5.5 to <5, then increased and mostly remained in the range





**Figure 2** REY<sub>BN</sub> patterns of experiments with basalt and DFC.

of 5–7 after 24 hr (Figs. S-2–S-4, Table S-4), similar to previous studies (Kraemer *et al.*, 2015). Some experiments reached pH values of 8 and higher. Cerium anomaly formation, especially under anoxic conditions, however, was not correlated with final solution pH (Figs. S-2, S-3). Leaching under anoxic and hypoxic conditions caused a generally slower pH increase over time (Fig. S-4). Over the observed pH range, DFOB speciation was dominated by H<sub>4</sub>DFOB<sup>+</sup> species with minor to equal contributions of H<sub>3</sub>DFOB (Fig. S-5).

Control experiments with DI and 0.01 mol/L HCl under anoxic conditions did not produce Ce anomalies in the leachate solutions (Fig. S-6).

## Discussion

The experiments indicate that leaching of redox-insensitive REY(III) by both DFOB and DFC is largely independent of actual  $pO_2$  as evidenced by very similar patterns between the individual experiments with the same run times. The patterns between the different experimental sets overlap, except for redox-sensitive Ce, implying that complexation of redox-insensitive trace elements with DFOB or DFC is solely a function of the complex stability constants, the mineralogical association of the REY, the texture of the rock, and the individual solubility of the host minerals, but *not* of oxygen. Due to the scarcity of available data for complexation of REY with DFC, the following discussion focuses on REY-DFOB interaction. Stability constants for REY-DFOB complexes are several orders of magnitude higher than those of mono- and dicarbonate REY complexes in seawater (Liu and Byrne, 1998), with log  $K_f$  of hexadentate complexes ranging from 10.09 for La to 15.19 for Lu at seawater ionic strength (Christenson and Schijf, 2011). In comparison, the hexadentate coordination of Fe<sup>3+</sup> results in a stability constant of 30.6 (DFOB; Martell and Smith, 2001). The increasing complex stability from light to heavy REY is observed, *e.g.*, in the leachates of the basalts and andesites, as the patterns show an increase from LREY<sub>BN</sub> towards MREY<sub>BN</sub> and HREY<sub>BN</sub>.

The only leachates with different REY<sub>BN</sub> patterns are of glassy MORB (Fig. 3d; flat REY<sub>BN</sub> without fractionation) and of granite (Fig. 1b; bell-shaped REY<sub>BN</sub>). The “MREY bulge”

observed in the granite experiment may be related to highly insoluble minerals present in felsic plutonic rocks. The leachates of glassy MORB show lower REY concentrations than those of the microcrystalline counterpart. As REY are incompatible with respect to most rock-forming igneous minerals, they are, in rocks with porphyritic/phaneritic textures, not incorporated into the crystal lattice but are preferentially located along grain boundaries and in the interstitial crystal spaces (Giese and Bau, 1994). During WRI, this REY pool is mobilised first since no dissolution of well-crystallised minerals is necessary. Divalent Eu is compatible with respect to, and incorporated into, Ca-rich plagioclase, and hence the REY pool on grain boundaries and in interstitial spaces is depleted in Eu (negative Eu<sub>CN</sub> anomaly). When this pool is mobilised during WRI, the solution inherits the Eu<sub>CN</sub> anomaly. In volcanic glass, however, Eu(II) and all REY(III) are homogeneously distributed, and hence no Eu<sub>CN</sub> anomaly can develop (Giese and Bau, 1994; Bach and Irber, 1998; Shibata *et al.*, 2006; Kraemer *et al.*, 2015).

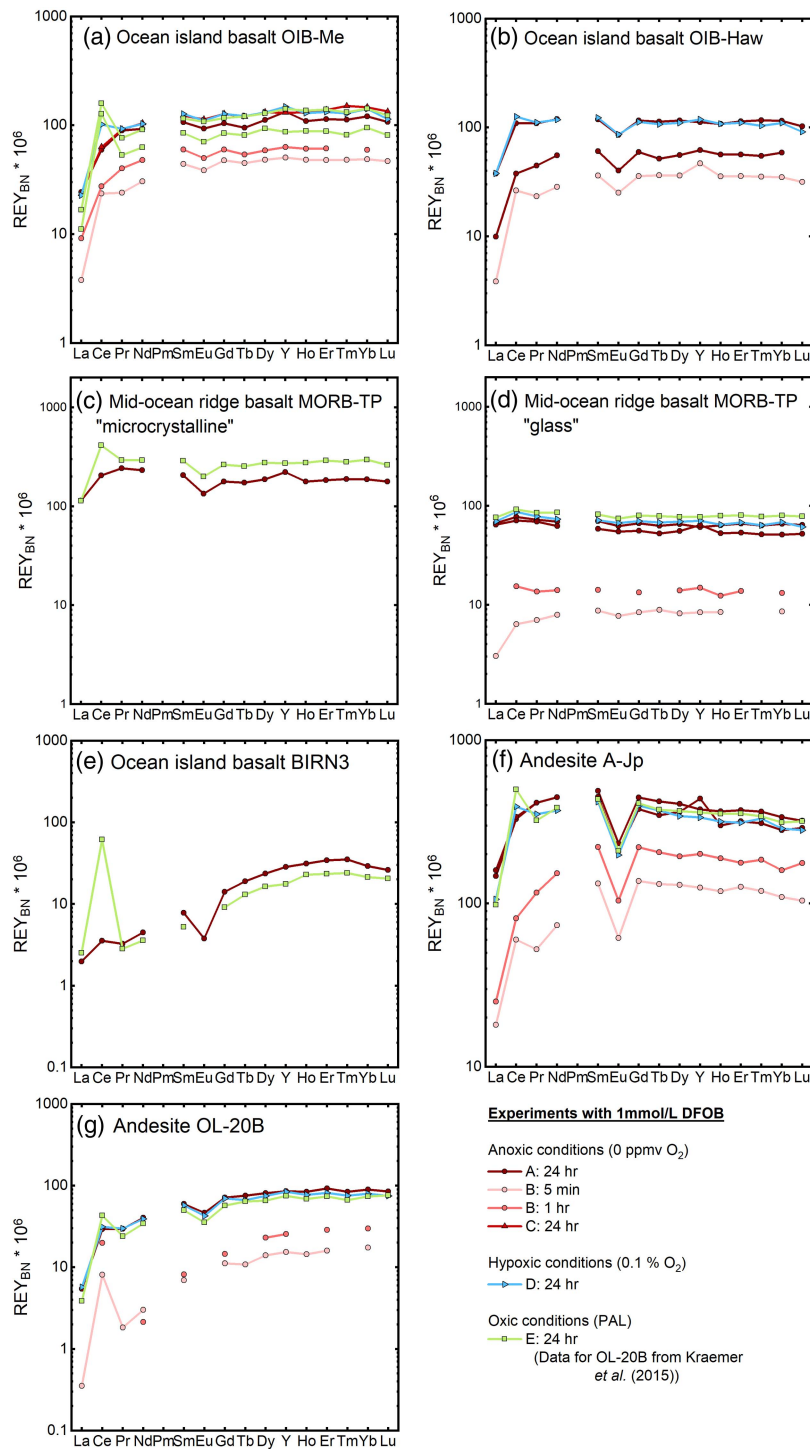
We conclude that  $pO_2$  neither influences the amount nor the fractionation of individual or total REY(III) mobilised from igneous rocks during WRI in the presence of DFOB or DFC. Our experiments demonstrate, in accordance with published data, that the solubilisation and complexation of isoivalent REY with DFOB or DFC is oxygen independent.

Leaching under hypoxic and oxic conditions leads to only minor fractionation of the Y–Ho geochemical twins, but pronounced fractionation was observed during short-term WRI under anoxic conditions (Fig. 4). The stability constants of Y and Ho with DFOB are similar (Christenson and Schijf, 2011) and no significant fractionation would be expected, in contrast to our results. Yttrium, however, appears to have a higher initial accessibility during WRI than Ho (Bau *et al.*, 1998), which could explain the Y fractionation during short-term WRI.

Cerium oxidation by the siderophore DFOB under oxic conditions has been demonstrated in several studies. Yoshida *et al.* (2004) conducted adsorption experiments of REY-DFOB complexes on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and *P. fluorescens* and found that Ce behaves markedly different from La(III) and Pr(III). They demonstrated the presence of Ce(IV)-DFOB in solution and concluded an oxidation of Ce(III) to Ce(IV) during DFOB complexation/adsorption. Siderophore-mediated oxidation was also demonstrated during oxic WRI with igneous rocks (Bau *et al.*, 2013; Kraemer *et al.*, 2015) and during scavenging onto Mn (hydr)oxides (Kraemer *et al.*, 2017) with the development of a positive Ce<sub>N</sub> anomaly.

In contrast to the log  $K_f$  of REY(III)-DFOB (between 10.09 ± 0.08 and 15.19 ± 0.02; Christenson and Schijf, 2011) and Ce(III)-DFOB hexadentate complexes (log  $K_f$  ≈ 11.59; back-extrapolated from Nd(III)- and Pr(III)-DFOB data of Christenson and Schijf, 2011), log  $K_f$  of Ce(IV)-DFOB was estimated to be significantly higher (25–30; Yoshida *et al.*, 2004) and thus comparable to Fe(III)-DFOB. The DFOB-mediated oxidation of redox-sensitive elements under oxic conditions was explained as follows:

- (i) a lowering of the oxidation potential by DFOB-complexation and rapid oxidation by ambient air (“air-oxidation”; Duckworth and Sposito, 2005) which increases the metal-ligand complex stability (Hernlem *et al.*, 1999; Kraemer *et al.*, 2014), and
- (ii) a disequilibrium between Ce<sup>3+</sup><sub>aq</sub> and Ce<sup>4+</sup><sub>aq</sub> at the mineral–water interface, where minute amounts of tetravalent Ce in solution are strongly complexed by DFOB, facilitating further disequilibrium and Ce<sup>4+</sup> regeneration by continuous oxidation of Ce<sup>3+</sup> to maintain redox



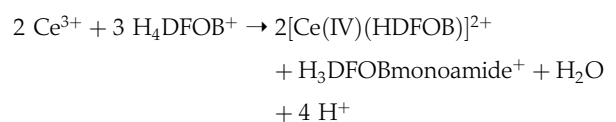
**Figure 3** REY<sub>BN</sub> patterns of leaching experiments with different igneous rocks. The letters A-E in the legend refer to different experiment runs. Details are listed in Table S-2.

equilibrium (“siderophore redox pump”; Bau *et al.*, 2013; Kraemer *et al.*, 2015, 2017).

Here, a Ce-LREY fractionation was observed even under anoxic conditions, although confined to short-term WRI. Clearly, the mechanisms proposed for Ce oxidation under (hyp)oxic conditions fail to explain this observation.

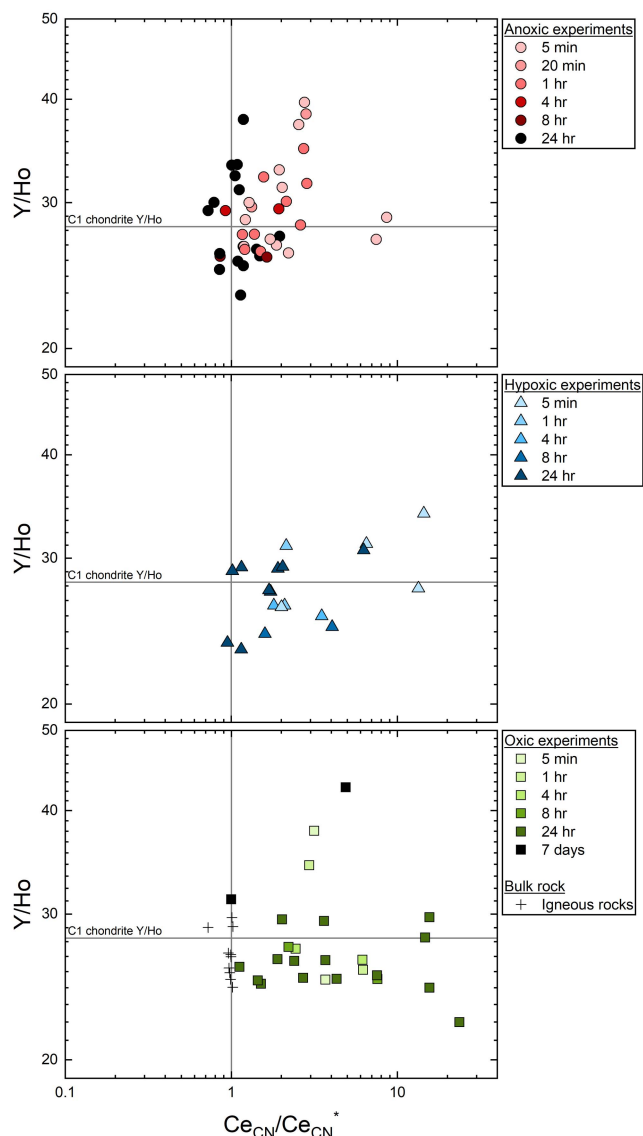
At the observed pH range, H<sub>4</sub>DFOB<sup>+</sup> is the dominant species in solution, and anoxic Ce oxidation may follow a reaction path similar to the *anoxic siderophore-promoted oxidation* of ferrous

Fe (Farkas *et al.*, 2001). The proposed reaction may be rewritten for a postulated anoxic Ce<sup>3+</sup> oxidation process:



The results show that Ce fractionation under anoxic conditions is limited to short-term WRI. Apparently, only “free” DFOB





**Figure 4** Graph of  $Ce_{CN}/Ce_{CN}^*$  vs. Y/Ho ratio for bulk rocks and leachates.

molecules may participate in this redox reaction. Hence, this process is limited to the first minutes of leaching, when the activity of “free”  $H_4DFOB^+$  is high and complexation with other metals with high complex stability (in particular Fe, which is present in excessive amounts in igneous rocks and which was also mobilised during the experiments; Figs. S-7–S-9, Table S-4) had not yet reduced the initial availability of this ligand. As WRI proceeds, the minute amounts of Ce(IV)-DFOB complexes formed under anoxic conditions are concealed by continuously increasing amounts of LREY(III)-DFOB complexes (including Ce(III)-DFOB) which effectively hide the Ce(IV) compounds in the  $REY_{BN}$  patterns.

We showed experimentally that complexation by biogenic ligands such as DFOB/DFC provides an *anoxic* and *hypoxic* pathway for the oxidation of  $Ce^{3+}$ , the subsequent oxidative decoupling of Ce from its neighbours in the REY series, and eventually the formation of positive Ce anomalies in normalised REY patterns of solutions produced during low-temperature WRI. We emphasise, however, that features of the Ce anomalies (e.g., height of peak or relative fractionation from Pr(III) or Nd(III)), cannot be used to distinguish between redox-driven and siderophore-driven fractionation.

In modern seawater, complexation of bioessential micro-nutrients (e.g., Fe(III)) is dominated by organic ligands, and previous studies have suggested that this ligand pool is dominated by siderophores (van den Berg, 1995; Gledhill *et al.*, 1998; Mawji *et al.*, 2008). Recent literature suggests that cyanobacteria may have produced siderophores for Fe(III) acquisition even before the Great Oxidation Event in the Palaeoproterozoic (Enzinger-Bleyle *et al.*, 2021). Today, siderophores also enable microorganisms to reduce toxic metal accumulation and to increase metal tolerance (e.g., Braud *et al.*, 2010), which might have been evolutionary advantageous also for early life. Neaman *et al.* (2005) argued that organisms have had to cope with low nutrient bioavailability since at least the colonisation of the land surface. In (modern) soils, siderophores are at least as abundant as in marine systems, with concentrations up to the mmol/L range (Nelson *et al.*, 1988), and significantly enhance the mobility of trace elements such as REY (Wiche *et al.*, 2017). More than 500 different natural siderophore compounds have been described from natural systems (Boukhalfa and Crumbliss, 2002); yet to date, it is not possible to estimate abundances of organic ligands during early periods of Earth’s history. In this regard, biosignatures may represent an important, yet unprecise tool.

As the different rock types showed very different REY fractionation patterns in the leachates, it is difficult to constrain REY patterns that are typical for WRI in presence of siderophores. The only distinct feature, apart from the Ce anomaly, is the occasionally very strong depletion of La (Bau *et al.*, 2013; Kraemer *et al.*, 2015, 2017; this study). Wang *et al.* (2020) identified La anomalies as fingerprints for methanotrophic activity. Therefore, we hypothesise that the observed La fractionation may also represent a characteristic biosignature of the involvement of siderophores in geochemical processes during WRI.

The fractionation of Ce in the presence of biomolecules as reported here sheds new light on the application of Ce anomalies as a geochemical proxy. Besides its well-established application as a qualitative redox proxy, Ce anomalies may have the potential to be used as a “bio-proxy”, indicating the presence of (siderophore-producing) biota, potentially even under anoxic conditions.

While oxidation by bio-ligands will further complicate the use of geochemical redox proxies, this opens an exciting venue for future studies and potential applications, particularly in the field of astrobiology.

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## Additional Information

Supplementary Information accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2227>.



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